Question 1: Antisymmetrizer and Slater determinants

The normalized, two electron ($n = 2$) wave function $\Phi(1,2)$ may be written using a Slater determinant

$$\Phi(1,2) = \frac{1}{\sqrt{n!}} \left|\phi_1 \overline{\phi}_1\right|, \tag{1}$$

or by using the anti-symmetrizer $\hat{\mathcal{A}}$

$$\Phi(1,2)' = \sqrt{n!}\, \hat{\mathcal{A}} \psi_1(1)\psi_2(2), \tag{2}$$

where the spin-orbitals ψ_i are given by $\psi_1(j) = \phi_1(j)\alpha(j)$ and $\psi_2(j) = \phi_1(j)\beta(j)$, with spatial orbital ϕ_1 and electron spin functions α and β. The anti-symmetrizer is given by a sum over all $n!$ permutations $\hat{P}$, with parities $(-1)^p$,

$$\hat{\mathcal{A}} = \frac{1}{n!} \sum_P (-1)^p \hat{P}. \tag{3}$$

For $n = 2$ this sum contains two permutations, $\hat{P} = \hat{\mathbf{1}}$ (the identity operator) and $\hat{P} = \hat{P}_{1,2}$, the operator that interchanges labels 1 and 2.

1a. Evaluate both $\Phi(1,2)$ and $\Phi(1,2)'$ and show that they are identical.

The antisymmetrizer satisfies, for each permutation $\hat{P}$

$$\hat{P}\hat{\mathcal{A}} = (-1)^p \hat{\mathcal{A}}. \tag{4}$$

1b. Verify this expression for $n = 2$ and $\hat{P} = \mathbf{1}$ and for $\hat{P} = \hat{P}_{1,2}$.

The antisymmetrizer also satisfies

$$\hat{\mathcal{A}}^2 = \hat{\mathcal{A}}. \tag{5}$$

1c. Prove Eq. (5) for arbitray n, using Eqs. (3) and (4).

Question 2: Coulomb and exchange integrals

The Coulomb integral is given by

$$J_{i,j} = \iint \frac{\psi_i(1)^* \psi_j(2)^* \psi_i(1)\psi_j(2)}{r_{12}} d\tau_1 d\tau_2.$$

The exchange integral is given by

$$K_{i,j} = \iint \frac{\psi_i(1)^* \psi_j(2)^* \psi_j(1)\psi_i(2)}{r_{12}} d\tau_1 d\tau_2.$$

Here, $\Psi_i(j)$ are spin-orbitals, and the integrals are over spatial and spin-coordinates

Hint(1): for any function of two electrons $f(1,2)$ one may use

$$\iint f(1,2) d\tau_1 d\tau_2 = \iint f(2,1) d\tau_2 d\tau_1 = \iint f(2,1) d\tau_1 d\tau_2.$$

The first step is allowed because the integration variable may be renamed. For the second equal sign we must assume that the order of integration does not matter.

Hint(2): for any functions of two electrons $f(1,2)$ and $g(1,2)$ one may use

$$\iint f(1,2)g(1,2)d\tau_1 d\tau_2 = \iint g(1,2)f(1,2)d\tau_1 d\tau_2,$$

and in general factors in a product of functions may be reordered.

2a. Show that $J_{i,i} = K_{i,i}$.

2b. Show that $J_{i,j} = J_{j,i}$.

2c. Show that $J^*_{i,j} = J_{i,j}$.

2d. Show that $K_{i,j} = K_{j,i}$.

2e. Show that $K^*_{i,j} = K_{i,j}$.

Question 3: Energy expressions for Slater determinants

Two closed shell electronic wave functions are given

$$\begin{aligned}\Phi_1 &= \frac{1}{\sqrt{2}}|\phi_1\overline{\phi}_1| \\ \Phi_2 &= \frac{1}{\sqrt{4!}}|\phi_1\overline{\phi}_1\phi_2\overline{\phi}_2|.\end{aligned}$$

The energy expression based on spin-orbitals (n-electron):

$$E = \sum_{i=1}^{n} h_{i,i} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}[J_{i,j} - K_{i,j}] + V_{N,N}.$$

The energy expression based on spatial orbitals for closed-shell configurations:

$$E = 2\sum_{k=1}^{n/2}\widetilde{h}_{k,k} + \sum_{k=1}^{n/2}\sum_{l=1}^{n/2}[2\widetilde{J}_{k,l} - \widetilde{K}_{k,l}] + V_{N,N}.$$

(The tilde indicates integrals over spatial orbitals.)

3a. What is $V_{N,N}$ and why is it boring here?

3b. Write out the energy expression for Φ_1 using the spatial-orbital expression.

3c. Derive the same expression for the energy of Φ_1 starting from the spin-orbital expression.

3d. Write out the energy expression for Φ_2 using the spatial-orbital expression.

3e. Derive the same expression for the energy of Φ_2 starting from the spin-orbital expression.